NOx Control for Compression Ignition Engines

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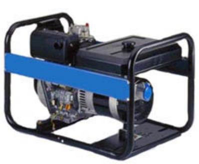
Reference: M7500

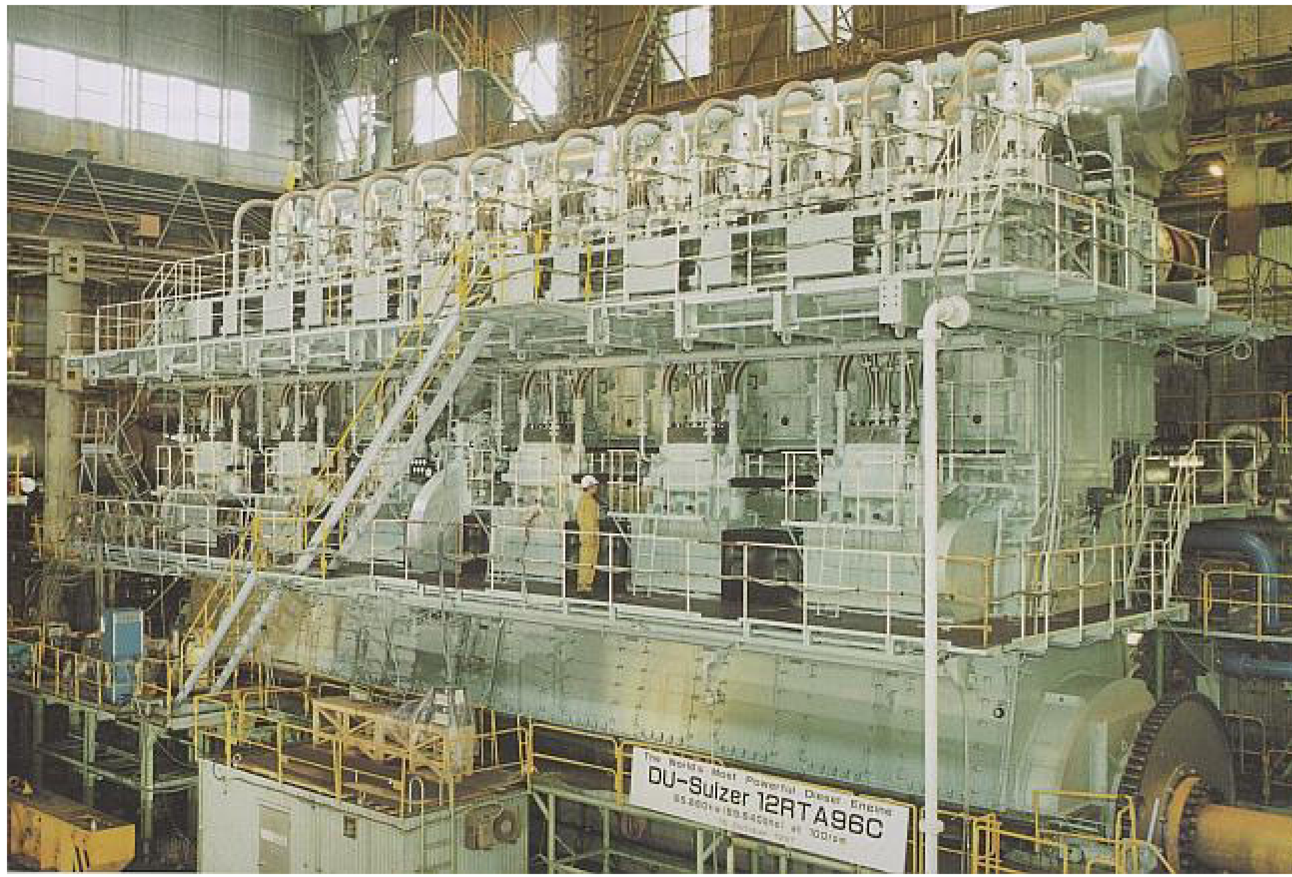
Technologies developed for NOx control for CI engines in transportation may offer performance and cost benefits for stationary applications.

- While there are differences in the characteristics of the exhaust streams, sufficient similarities permit sharing of technology.
- Dual mode technologies and hydrocarbon-based SCR, being developed for transportation, may be, in fact, easier to deploy in stationary applications.
- There could be synergies in the supply of urea if the infrastructure needed for transportation does develop.
- System-level and component-level modeling tools are available that are useful to both transportation and stationary applications.

Compression ignition engines for power generation range in size from 1 to 125,000 kW and 20 to 50% thermal efficiency.

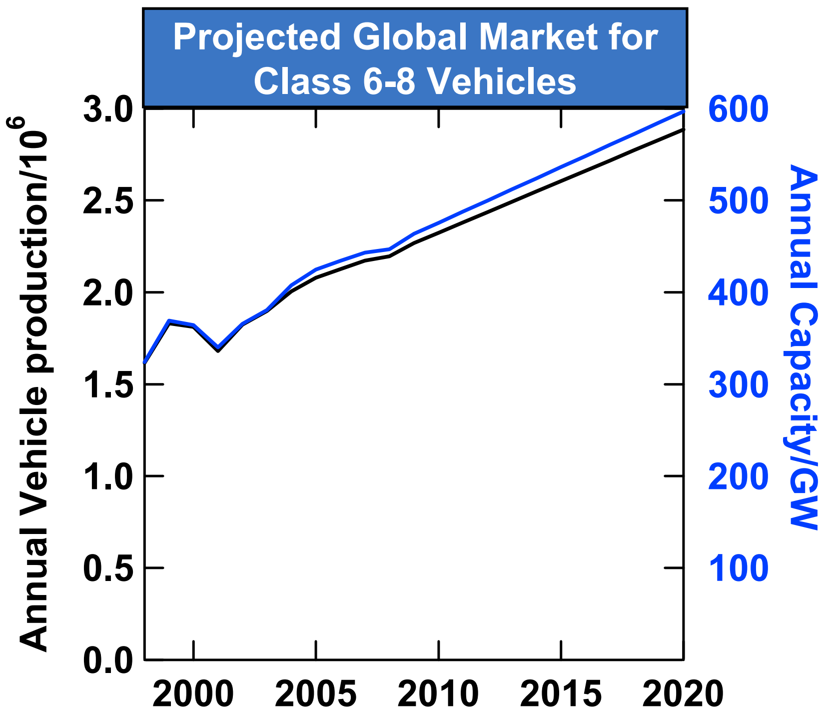


Yanmar L 100



Wartsila NSD (Sulzer) 12 RTA96-C two-stroke diesel engine

The scale and operating constraints of the transportation industry should benefit stationary applications...



Source: Global Insight

	Trucks	Power
2010 US NOx levels/ g kWh^{-1}	0.2	0.15*
Space Velocity/ h^{-1}	20,000 to 50,000	1000 to 10,000
Installed costs/ $ kW^{-1}	10 to 40	5-10
Expected lifetime/ h	10,000	>24,000

* 0.1 g/kWh = 0.1 lb/MMBTU

… with implications for fuels, sensors, infrastructure, etc.

The exhaust streams from CI engines are typically leaner and faster flowing than those from process heaters and turbines.

Exhaust Characteristic	CI 4-Stroke	CI 2-Stroke	Flue gas
Catalyst inlet temperature/°C	200-350	350-400	200-500
Flow rate/kg h^{-1} kW^{-1}	4-9 pulsatile	3-9 pulsatile	1.4-4 continuous
O_2/%	10-12	10-15	2-15
NO_x/ppm	100-2500	90-1500	20-500
HC/ppm	<50	<500	<10*

* Condensed fuels yield higher emissions of hydrocarbons

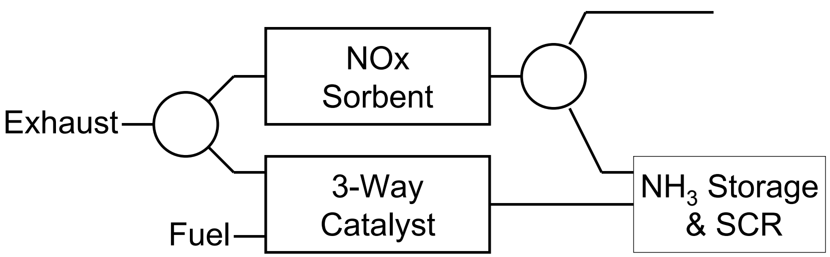
Sources: Bosch Automotive Handbook, Dieselnet, Cormetech, Wartsila, MAN, TIAX analysis

Four types of aftertreatment processes are being actively pursued for NO_x abatement in transportation applications.

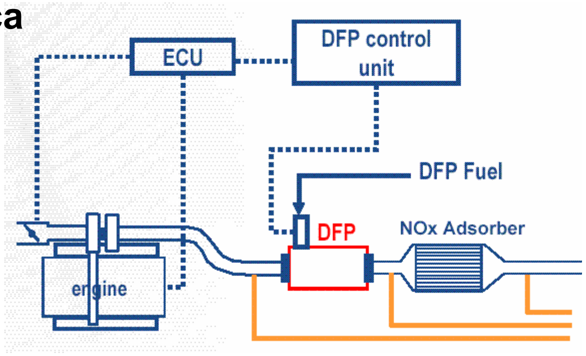
Process	Overall Chemistry	Characteristics
Urea SCR	$NO_x + NH_3 + O_2 = N_2, H_2O$	• 80-95% conversion • Requires additional reagent • Requires excellent metering control • Sulfur tolerant
HC SCR	$NO_x + CH_y + O_2 = N_2, H_2O, CO_2$	• 40-60% conversion • Can use fuel or reformed fuel • 1-5% fuel economy penalty • Excess reductant does not make NO_x
Lean NOx Trap	$NO_x + O_2 + BaO = BaNO_3$ $BaNO_3 + CH_y = N_2, H_2O, CO_2, BaO$	• 70-95% conversion • Sensitive to sulfur • Needs swing bed for highest fuel efficiency
Dual mode	$NO + O_2 = NO_2$ $NO_2 + C = N_2, CO_2$ $NO_x + BaO = BaNO_3$ $BaNO_3 + CH_y = N_2, H_2O, CO_2, BaO$	• 70-90% conversion • Sensitive to sulfur • Comparatively compact (single reactor, multiple beds)

More complicated modes of NOx abatement have been proposed to take advantage of known chemistries of emission control devices.

Umicore (dmc²)



Catalytica

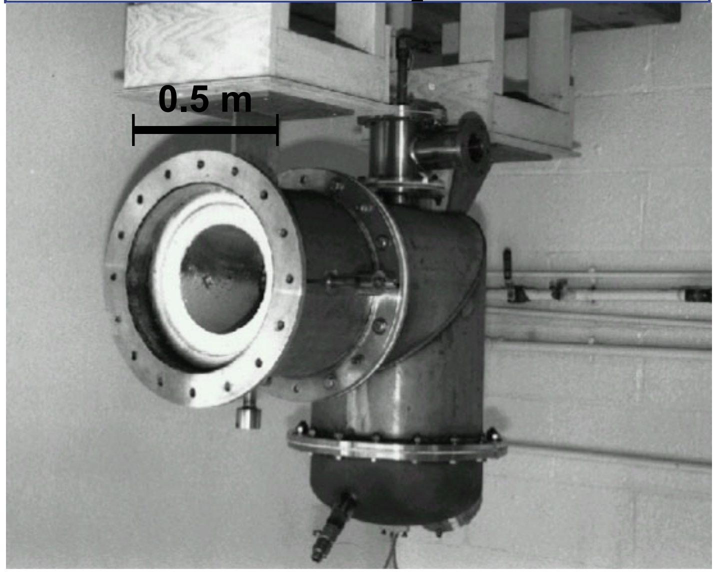


- Use a 3-way catalyst under rich conditions to generate NH_3
- Use a NO_x sorbent to scavenge NO_x during lean operation
- Periodically react the stored NOx and stored NH_3

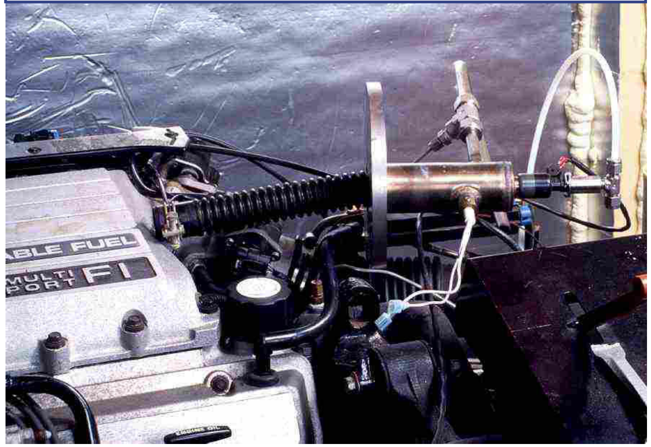
- Fuel reformer produces H_2 and CO
- Reformate fed periodically to an LNT to regenerate it

The NOx abatement could also be configured to use renewable reducing agents like ethanol or other biomass-based hydrocarbons.

A 750 kW catalytic partial oxidation reactor developed by TIAX staff that can be fueled with ethanol or other bio-fuels to produce H_2 and CO



A 1 kW catalytic partial oxidation reactor developed by TIAX staff for cold start of ethanol-fueled engines

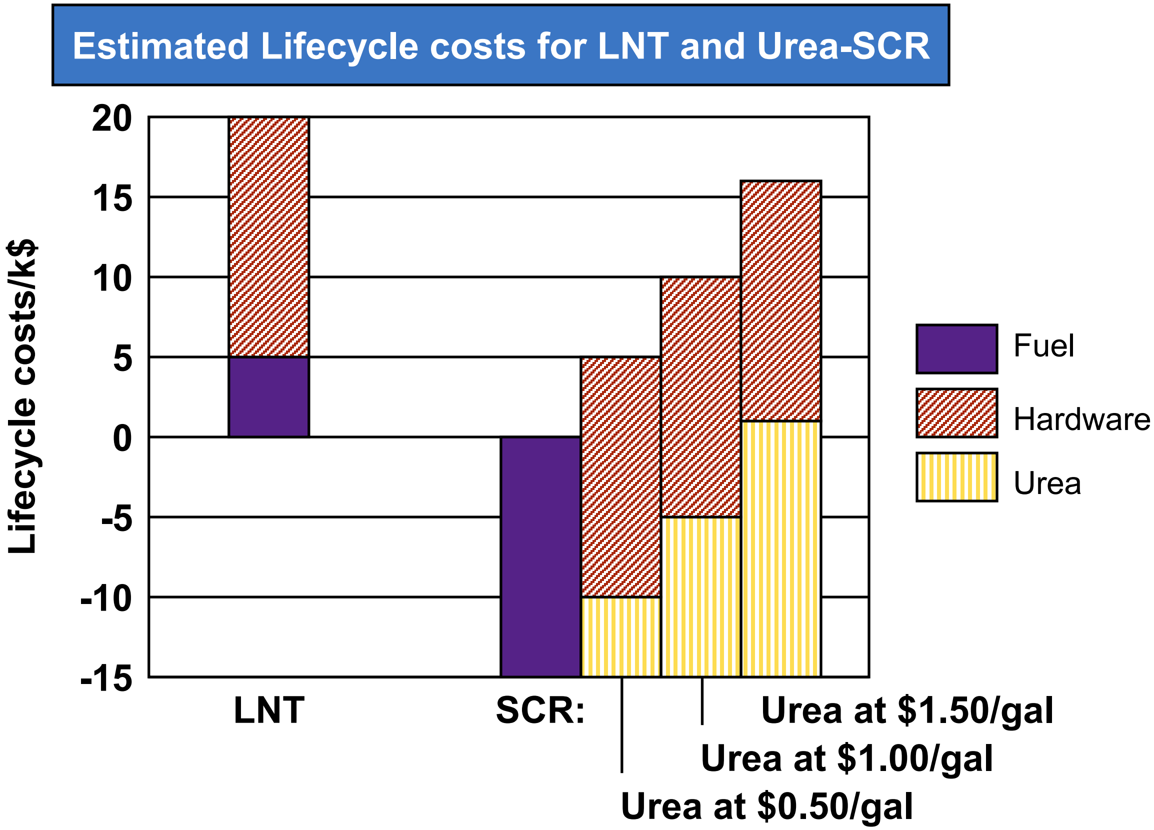


Our recent analysis* suggests that, short of a breakthrough in LNT’s, urea SCR could be viable if infrastructure issues are resolved.

- **Economics also generally favor the SCR/urea technology over the NOx adsorber technology in the near-term if early NOx adsorbers have a high fuel penalty (˜5%) and a higher initial incremental cost.**
- **Economics will continue to favor the SCR/urea technology over the NOx adsorber technology for most applications of long-haul and vocational trucks in the long-term unless LNT’s become more frugal.**
- **Provision of urea is both possible and economically reasonable if strong signals regarding manufacturers’ intentions to provide SCR-equipped trucks are sent to truck operators and other stakeholders no later than mid-2004**

* TIAX Urea SCR Infrastructure Study for the Engine Manufacturers’ Association, 2003

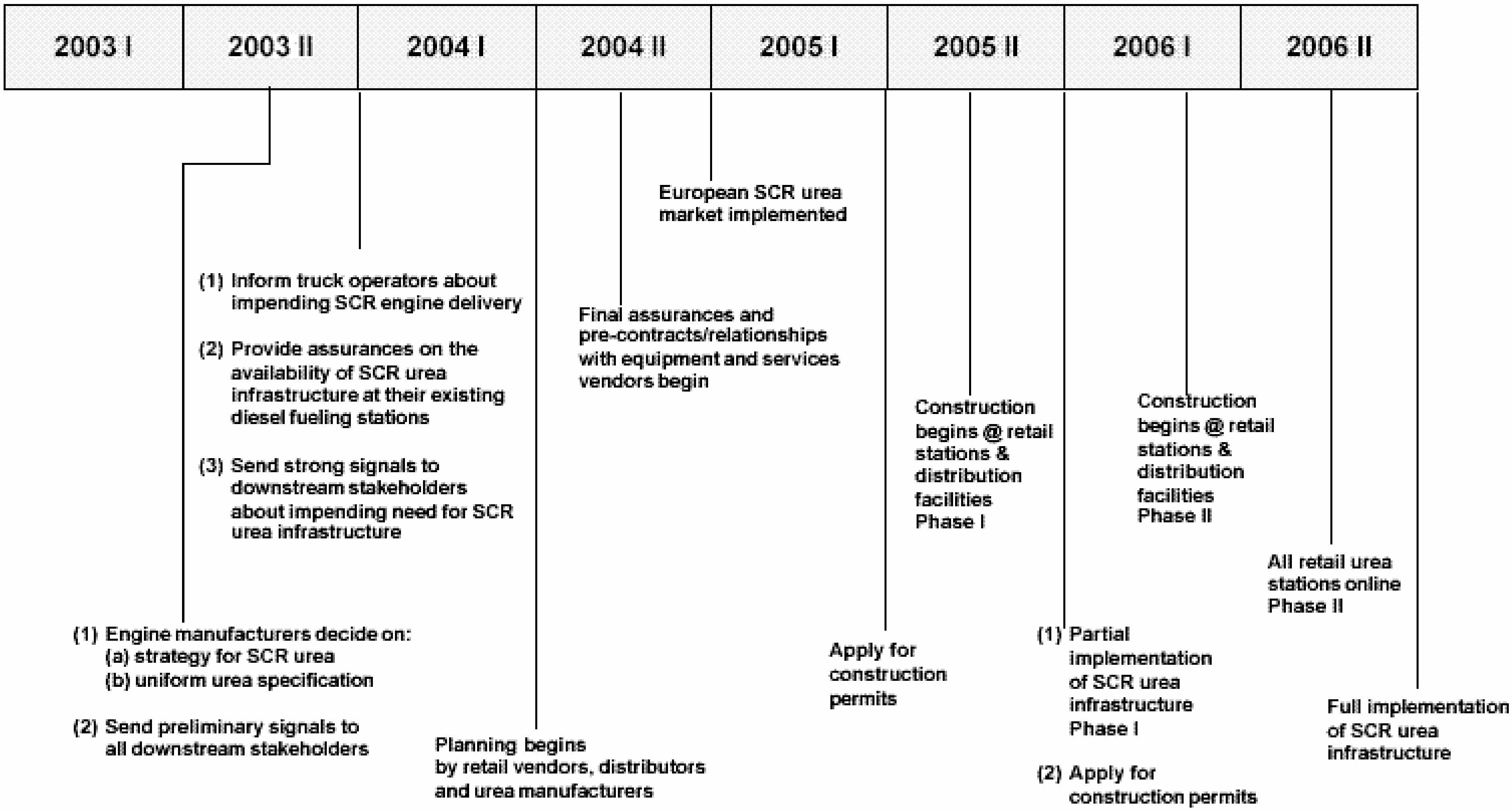
For engines requiring "only" 90% NOx conversion, SCR appears to be the most economical path forward.



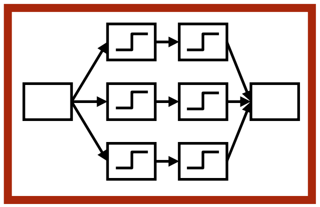
- Urea-SCR obviates the need for high EGR and thus gives a fuel economy benefit (high peak temperature gives low soot and high efficiency)
- This strategy works in Europe, where allowable NOx limits will be 10-fold greater than in the US

Source: DaimlerChrysler (DEER 2003)

Members of the urea-SCR value chain need surety in the very near future for this technology to be deployed in the US to satisfy the 2007 regulations.

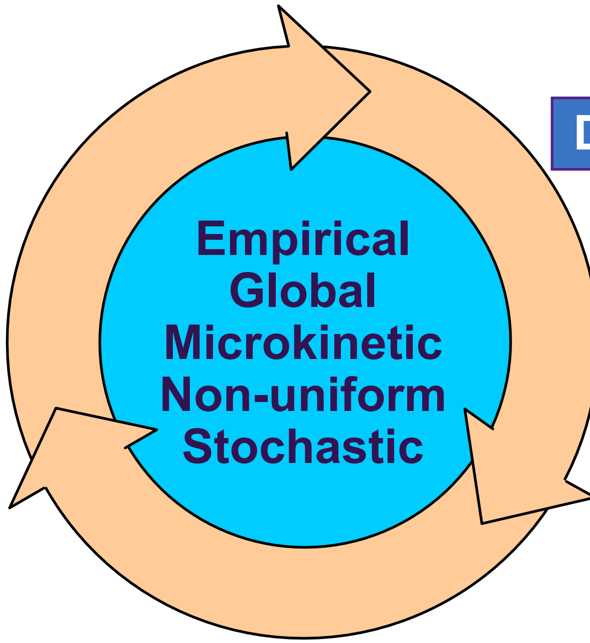


The three phases of emissions control each needs a different kind of model to extract the most utility from the available information.

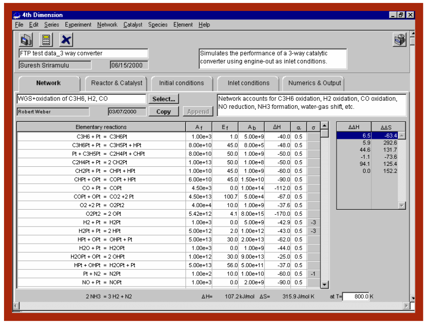


Model reduction

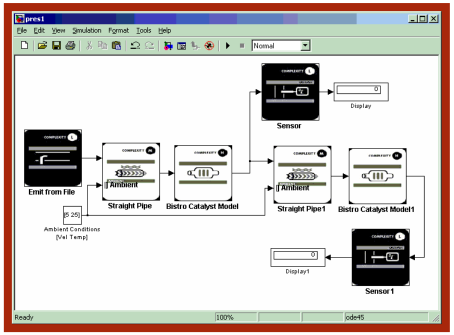
Use



Discovery



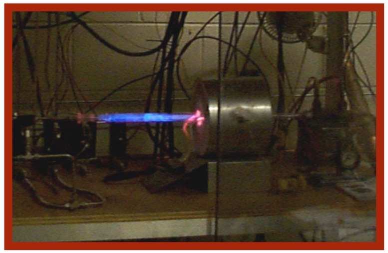
Kinetics modeling



System simulation

Design & Manufacture

Technology Assessments
Market Assessments
IP Monetization



Rapid calibration

Conventional, global catalyst models represent data over limited ranges and afford no cross-system learning.

- In conventional models the parameters in the empirical rate expressions are just fitting coefficients and have no physical meaning.
- Moreover, the form of conventional models is not well adapted to describe transient performance—neither startup nor acceleration.
- Therefore conventional models cannot be tied to the properties or formulation of the catalysts and must be retuned from scratch for each new system.

Example of a conventional expression used to describe the rate of a reaction catalyzed by a catalytic converter

Functional form forces numerical correlation between parameters, making it difficult to determine accurate values

Based only on observable species, ignores available information about surface species

$$r = \frac{k \cdot K \cdot P_{CO} P_{O_2}}{1 + K \cdot P_{CO}}$$

Assumes that adsorption is equilibrated and that surface species are in steady state, precluding accurate description of fast transients

Advanced microkinetics models provide insight into catalyst performance, including degradation, that bears directly on cost, reliability and control.

- Microkinetics models are sets of coupled differential equations built from a fundamental understanding of the chemical steps that occur on the surface of the catalyst.
- The models can be accurate over a wide range of conditions and are intrinsically capable of representing transients.
- The generality and extensibility of microkinetics models allow simulations that can lead to new catalysts which are cheaper and more robust (different metals, lower loading, use protocols).
- Extending a microkinetics model to include other sorts of reactions, notably catalyst degradation, is straightforward.
- Since the models represent many levels of performance, they can be interrogated to devise model-based control.

Microkinetics network for oxidation of propene

$C_3H_6 + Rh = C_3H_6Rh$
$C_3H_6Rh + Rh = C_3H_5Rh + HRh$
$Rh + C_3H_5Rh = C_2H_4Rh + CHRh$
$C_2H_4Rh + Rh = 2\ CH_2Rh$
$CH_2Rh + Rh = CHRh + HRh$
$CHRh + ORh = CORh + HRh$
$CO + Rh = CORh$
$CORh + ORh = CO_2 + 2\ Rh$
$O_2 + Rh = O_2Rh$
$O_2Rh + Rh = 2\ ORh$
$H_2 + Rh = H_2Rh$
$H_2Rh + Rh = 2\ HRh$
$HRh + ORh = OHRh + Rh$
$H_2O + Rh = H_2ORh$
$H_2ORh + ORh = 2\ OHRh$
$HRh + OHRh = H_2ORh + Rh$
.
.
.

Reactions are not assumed to be equilibrated or irreversible

Reaction rates are expressed in Arrhenius form, $r = A \exp(-E_a/RT)$, with parameters derived from transition state theory or fundamental measurements

We developed Bistro™, a platform for creating microkinetics-based models that incorporate much of the credo of catalysis.

Calculate transient performance of chemical reactor using MATLAB.

Export models to Runway™

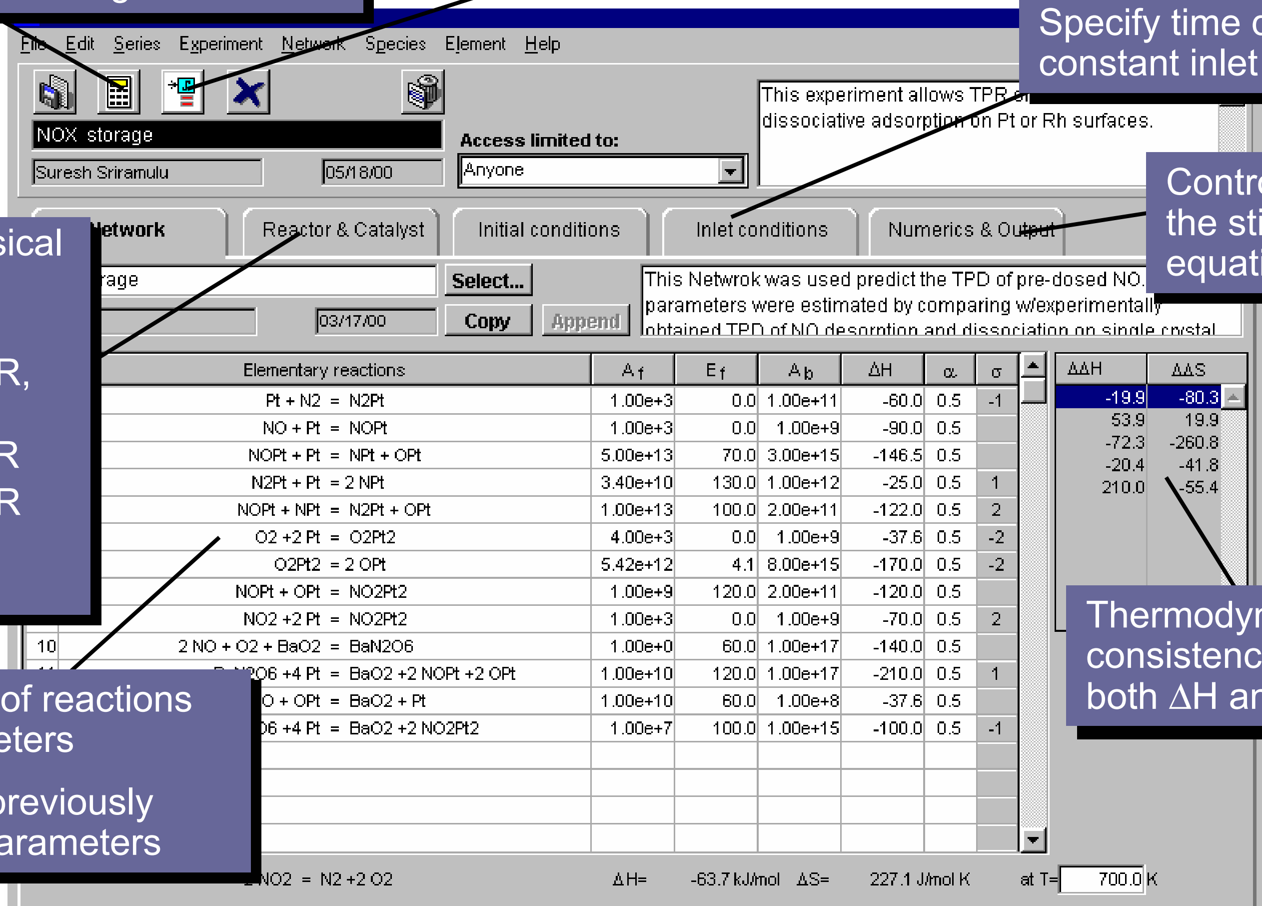
Specify time dependent or constant inlet conditions

Control solution of the stiff differential equations.

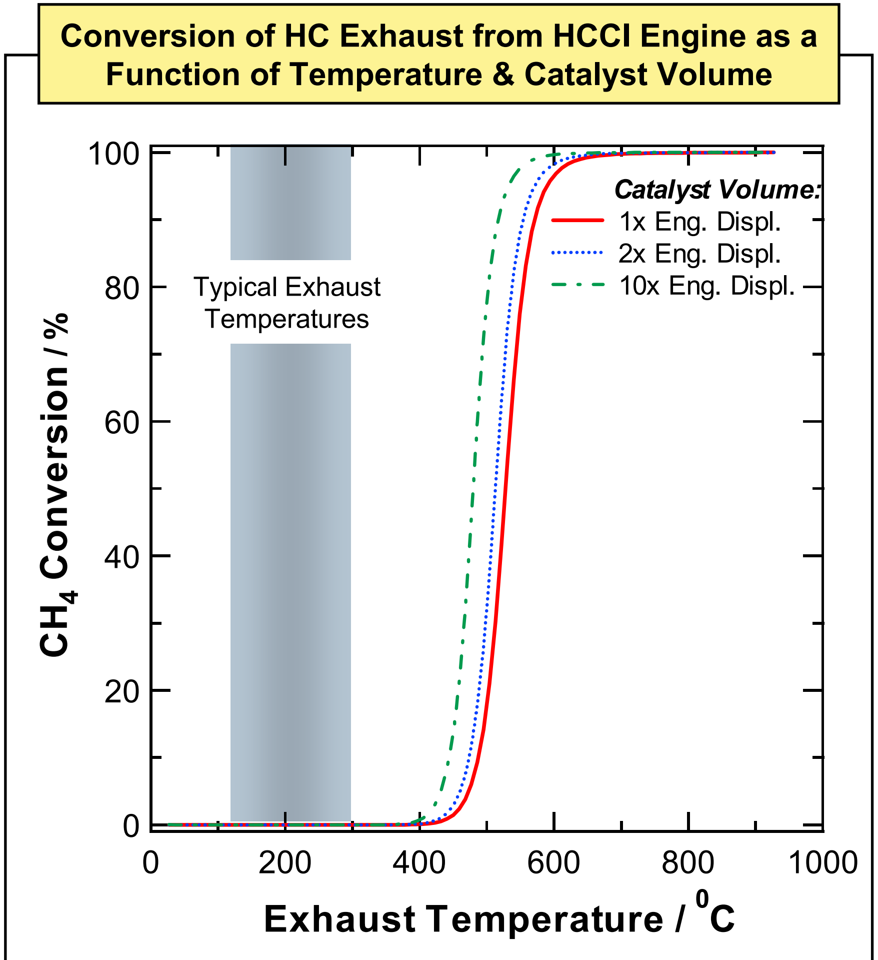
- Thermo-physical properties
- Adiabatic
  - CSTR, PFR, Film PFR
- TPD and TPR
  - CSTR, PFR
  - Sensitivity analysis

- Easy entry of reactions and parameters
- Re-use of previously validated parameters

Thermodynamic consistency check of both ΔH and ΔS



Our modeling suggests that ultralow NO_x HCCI engines may stumble over HC control because of their low exhaust temperatures.



- Kinetics model based on NREL work
- Assumed a Pt-based catalyst with loading of 60g/ft^3 Pt with 1.5 nm dia. Pt particles
- Exhaust conditions:0.5 % CH_4, 7 % O_2, 0.5 % CO
- Assumed fast heat transfer between catalyst and gas
- Simulation corresponds to an experiment with a temperature programmed reactor.

The power industry might consider formal, yet frugal, ways of facilitating innovation transfer of emission solutions developed for transportation.

- What new reagents, including renewables should be considered?
- What new chemistries are available?
- Could multiple effect devices be employed?
- Would Web Services permit economies in the value chain?